Polymer 51 (2010) 2576–2584

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Characterization of spatial inhomogeneities and dynamic properties of random cross-linked polystyrene networks by dynamic light scattering

Franziska Krahl*, Volodymyr Boyko [1], Karl-Friedrich Arndt

Department of Chemistry, Physical Chemistry of Polymers, Technische Universität Dresden, 01062 Dresden, Germany

ARTICLE INFO

Article history:
Received 16 November 2009
Received in revised form
16 March 2010
Accepted 9 April 2010
Available online 18 April 2010

Keywords:
Inhomogeneity
Dynamic light scattering
Random cross-linking

ABSTRACT

The network inhomogeneity and the cooperative motion of the network chains of random cross-linked poly(styrene-*co*-maleic anhydride) gels were investigated by dynamic light scattering. Measurements were performed for gels in the preparation state as well as in the swelling equilibrium. Network inhomogeneities and cooperative motion were analyzed at varying the cross-linker concentration and the polymer volume fraction. While the cross-linker concentration has only a minor influence on the inhomogeneity and the diffusion constant D_{coop}, the polymer volume fraction clearly influences both measured properties. The concentration dependence of D_{coop} can be well described by a power law, as known for semi-dilute polymer solutions. In the preparation state the networks appear homogeneous, exhibiting dynamic contributions to the scattering intensity of 70–90%. Swollen to equilibrium stage, significant heterogeneities emerge, reducing the dynamic contributions to 10–20%.

1. Introduction

Chemically cross-linked polymeric networks can be prepared either by free-radical copolymerization of monomers and cross-linking agents (cross-linking polymerization), or by cross-linking pre-build polymers (polymer cross-linking or random cross-linking). During the cross-linking process inhomogeneities are introduced into the network [1]. As a result, the networks structure, topologically frozen by the cross-linking, shows e.g. a spatial heterogeneity of the network density [2]. One characteristic of gels is the so-called speckle pattern: the scattering intensity depends on the sample position, usually attributed to the presence of inhomogeneities [3–14]. Thus, a gel can be regarded as non-ergodic medium because a time-averaged measurement at one sample position will not, in general, be equivalent to an ensemble-averaged measurement. It should be noted that nonergodicity is not related to inhomogeneities, but to topological restrictions of chain motion [15].

The degree of inhomogeneity is affected by the way of cross-linking. Cross-linking polymerization usually results in highly heterogeneous networks due to extensive cyclization and multiple cross-linking reactions at the early stage of the reaction [16,17]. Mainly compact clusters or microgel particles are formed during this stage, which are later connected to each other. The gel structure can be regarded as an assembly of these clusters tied together with low cross-linking density. Extensive studies on inhomogeneity of networks obtained through this route were performed using neutron and light scattering [4,18–28].

In contrast, only few investigations were reported on polymer cross-linked systems. Such systems can be obtained by radiation induced process [29–31] or by chemical reaction of reactive groups present in the polymer chain [32–34]. Comparisons of networks obtained by monomer cross-linking and by cross-linking of semi-dilute polymer solutions revealed that the structure of the latter appears to be more homogeneous [11,14,35]. Recently, using small-angle neutron scattering (SANS), it could be shown that tetra-arm polyethylene glycol chains, cross-end coupled, yield networks without defects [15,36,37]. Furthermore, a speckle-free gel was reported by Ngai et al. synthesized by [2 + 2] photocycloaddition of coumarin groups present in a poly(methyl methacrylate) polymer [38,12].

However, it is not clear which physical quantity can be used to define the degree of inhomogeneity out of scattering experiments. Several aspects are usually attributed to the presence of inhomogeneities: a) Strong upturn in the scattering intensity at low q region in SANS measurements [2]. b) non-uniformity of the scattering intensity over the sample position (speckle pattern). Strong fluctuations are referred to a high degree of inhomogeneity. c) Excess scattering of gels over the scattering of polymer solutions [39]. d) High values of the ensemble-averaged scattering. e) Strong mean-square refractive index fluctuations [14].

---

* Corresponding author. Tel.: +49 351 463 32492; fax: +49 351 463 39055.
E-mail address: franziska.krahl@tu-dresden.de (F. Krahl).

[1] Present address: Polymer Physics, BASF SE, 67056 Ludwigshafen, Germany

0032-3861/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2010.04.025

Beside this, the ratio of the dynamic fluctuations to the total scattering intensity can also be used to reflect the extent of inhomogeneity [40]. Since static contributions are always present in polymer gels, this ratio will never reach unity. Furthermore, inhomogeneities inherently occur in polymer gels due to the presence of cross-links [36]. However, if the dynamic fluctuations dominate, a homogeneous network structure seems more likely.

In this paper, inhomogeneities of random cross-linked networks based on a poly(styrene-*co*-maleic anhydride) copolymer (SMA) were studied by dynamic light scattering (DLS). Using ethylene glycol (EG) as bi-functional cross-linker, SMA can be cross-linked by esterification of maleic anhydride (MA) units. The influence of polymer and cross-linker concentration on the inhomogeneity of the resulting networks will be discussed. All gels were investigated in the preparation state as well as in the swelling equilibrium, to show how the swelling state influences the network heterogeneity. It will be shown, that the ratio of the dynamic contributions to the scattering intensity is an excellent tool to quantify the degree of inhomogeneity.

2. Theoretical background

A single dynamic light scattering measurement provides the time-averaged scattering intensity $\langle I(q)\rangle_T$ and the intensity–intensity time correlation function $g_T^{(2)}(q,t)$, with $\langle\ldots\rangle_T$ indicating a time-average [3]:

$$g_T^{(2)}(q,t) = \frac{\langle I(q,0)I(q,t)\rangle_T}{\langle I(q,0)\rangle_T^2} \tag{1}$$

t is the delay time and q is the scattering vector: $q = (4\pi n/\lambda_0)\sin(\theta/2)$, with n, λ_0 and θ being the refractive index of the medium, the vacuum wavelength of the incident beam and the scattering angle, respectively.

$g_T^{(2)}(q,t)$ can be converted to the first-order electric field correlation function $g_T^{(1)}(q,t)$, and for monodisperse samples the diffusion coefficient D can be obtained from the decay rate Γ [41]:

$$g_T^{(1)}(q,t) = \sqrt{g_T^{(2)}(q,t)-1} = e^{-\Gamma t} \quad \Gamma = Dq^2 \tag{2}$$

for non-ergodic systems such as glasses or gels, $\langle I(q)\rangle_T$ is sample position dependent finding its expression in the so-called speckle pattern. Two components contribute to $\langle I(q)\rangle_T$:

$$\langle I(q)\rangle_T = \langle IF(q)\rangle_T + I_C(q) \tag{3}$$

with $\langle I_F(q)\rangle_T$ being the time-average of the fluctuating component arising from dynamic concentration fluctuations and $I_C(q)$ being the time independent static component origin from the frozen-in density fluctuations [42]. The separation of $\langle I(q)\rangle_T$ into its two components can be performed by the partial heterodyne approach. $\langle I(q)\rangle_T$ and $g_T^{(2)}(q,t)$ are measured at different sample positions. For the short-time limit an apparent diffusion coefficient D_{app} is related to $g_T^{(2)}(q,t)$:

$$D_{\mathrm{app}} = -\frac{1}{2q^2}\lim_{t\to 0}\ln\left(g_T^{(2)}(q,t)-1\right) \tag{4}$$

For gels D_{app} varies with sample position in the range of $D_{\mathrm{coop}}/2 < D_{\mathrm{app}} < D_{\mathrm{coop}}$, with D_{coop} being the cooperative diffusion coefficient describing the ensemble-averaged cooperative motion of the network chains. D_{coop} and $\langle I_F(q)\rangle_T$ are obtained by plotting D_{app} and $\langle I(q)\rangle_T$ of all measured sample positions according to Eq. (5) [2]:

$$\frac{\langle I(q)\rangle_T}{D_{\mathrm{app}}} = \frac{2\langle I(q)\rangle_T}{D_{\mathrm{coop}}} - \frac{\langle I_F(q)\rangle_T}{D_{\mathrm{coop}}} \tag{5}$$

some studies indicate that also dynamic inhomogeneities exist in gels that can be physically interpreted as the differences of the molecular environment, such as local cross-linking density and segmental concentration [13]. They become obvious for gels with rather high cross-linking density. For the present study $\langle I_F(q)\rangle_T$ was treated as being position independent.

3. Experimental section

3.1. Materials

For the gel synthesis commercially available poly(styrene-*co* maleic anhydride) from Sigma–Aldrich (Germany) was used. The maleic anhydride content was determined by ^{1}H NMR-spectroscopy to 14 mol%. Distortionless enhancement by polarisation transfer (DEPT)-NMR measurement verified a random distribution of maleic anhydride and PS. Ethylene glycol and 4-(dimethylamino) pyridine (DMAP) were purchased from Merck-Schuchardt (Germany). Dioxane from VWR International (Germany) was stored over KOH and was freshly distilled before used.

3.2. Sample preparation

Poly(styrene-*co*-maleic anhydride) networks (PS-*co*-MA) were prepared by cross-linking SMA with EG in dioxane using DMAP as catalyst. The reaction solutions were prepared by mixing appropriate amounts of individual stock solutions of the reactants. Four gel series based on different SMA concentrations were made: 7.5, 10, 12.5, and 15 wt.%. The concentration of EG was varied in stoichiometric ratios of MA units to EG from 1:0.1 to 1:2, e.g. the gel 10_0.5 contains 10 wt.% SMA with a ratio of MA to EG of 1:0.5. 2 mol % of DMAP corresponding to the amount of MA groups were used. To illustrate the synthetic procedure, details for the preparation of the gel 10_0.5 are described below.

To 12.54 g of a 12 wt.% stock solution of SMA in dioxane 0.481 ml EG stock solution ($c = 132$ g/l) and 0.459 ml DMAP stock solution ($c = 11$ g/l) were added and completed with 1.54 ml dioxane so that the SMA concentration was adjusted to 10 wt.%. The reaction solution was filtered directly into the reaction tubes using 5 μm PTFE membrane filter (Rotilabo, Carl-Roth, Germany).

For investigations of the preparation state the reactions were carried out in the light scattering vials (⌀ = 8 mm). For measurements in the swelling equilibrium gels were prepared in polypropylene (PP) tubes with the same diameter as the light scattering vials. Contrary to glass tubes the samples can easily be removed out of PP tubes. The vials and PP tubes were plugged and immersed in a container which was filled with a low level of dioxane to avoid solvent evaporation. The gelation reaction was carried out at 70 °C. Reaction times vary among different samples. After macroscopic gelation was observed (tilt test), the gels were stored for another period of time at 70 °C, which equals the gelation time, e.g. if the gelation occurred after 4 days the gel were left another 4 days at 70 °C.

Investigations in the preparation state were performed without further treatment (no extraction). For experiments in the fully swollen state the gels were removed out of the PP tubes and swollen in dioxane for several weeks. The swelling agent was changed several times. The swollen samples were subsequently loaded in 18 mm test tubes.

3.3. Static light scattering

Weight average molecular weight (M_w) and radius of gyration (R_g) of SMA were determined by static light scattering (SLS) measurements in dioxane. The measurements were carried out at

25 °C in the angular range of 20–150° using a modified FICA 50 (SLS Systemtechnik Langen, Germany) equipped with a He/Ne-Laser (632.8 nm) as light source. Toluene was used as calibration standard. The scattering intensities of SMA solutions of 1–5 g/l were measured and evaluated according to Zimm. Prior to the measurements the solutions were filtered using 0.22 μm PTFE membrane filter (Rotilabo, Carl-Roth, Germany).

3.4. Dynamic light scattering

Dynamic Light Scattering (DLS) measurements were carried out on commercial laser light scattering spectrometer (ALV/DLS/SLS-5000) equipped with an ALV-5000/EPP multiple digital time correlator and laser goniometer system ALV/CGS-8F S/N 025. A helium-neon laser (Uniphase 1145P, output power of 22 mW and wavelength of 632.8 nm) was used as the light source. The time-averaged scattering intensity ($\langle I(q)\rangle_T$) and the time-averaged intensity correlation function ($g^{(2)}(q, t) - 1$) were measured at a scattering angle of 90° ($q = 2.0 \times 10^{-2}$ nm^{-1}) at 25 °C. Therefore, for discussion, $\langle I\rangle_T$ and $\langle I_F\rangle_T$ were used instead of $\langle I(q)\rangle_T$ and $\langle I_F(q)\rangle_T$. Ensemble averaging was performed by collecting $g^{(2)}(t)-1$ and $\langle I\rangle_T$ at 100 different sample positions by rotating the test tube with a self-made rotation unit.

Angular dependent measurements in a range of 30–120° for exemplary samples revealed that the characteristic decay rate Γ is proportional to q^2. The relaxation can therefore be considered as purely diffusive and measurements at one scattering angle are sufficient to determine D_{coop}.

4. Results and discussion

4.1. Poly(styrene-co-maleic anhydride)

M_w and R_g of SMA were determined by SLS to 1.98×10^5 g/mol and 21 nm, respectively. Additional size exclusion chromatography measurements gave M_w and M_n of 1.94×10^5 g/mol and 9.2×10^4 g/mol, respectively, yielding a polydispersity of 2.1.

Since the minimum concentration required for a network formation is identical to the overlap concentration c^*, it is of interest to determine this value for SMA in dioxane. c^* denotes the crossover between dilute and semi-dilute solution where the individual polymer coils start to overlap. Knowing M_w and R_g of a polymer-solvent system, c^* an be estimated [43]:

$$c^* = \frac{3M_W}{4\pi N_A (R_g)^3} \tag{6}$$

where N_A is Avogadro's number. For SMA used in this study Eq. (6) results in c^* of 8.5 g/l. This corresponds to a polymer volume fraction of $\phi_B = 7 \times 10^{-3}$ (~1 wt.%).

Another way to estimate c^* is to measure $\langle I\rangle_T$ of SMA solutions with different concentrations as shown in Fig. 1. With increasing polymer concentration $\langle I\rangle_T$ increases up to maximum value. The concentration at which $\langle I\rangle_T$ reaches maximum is c^*. Below c^* the polymer is in dilute state and with increasing concentration the amount of scattering centers increase, causing an increase in $\langle I\rangle_T$. Above c^* $\langle I\rangle_T$ decreases with increasing concentration due to an increase in osmotic compressibility [44]. Fig. 1 reveals an overlap concentration of $c^* \sim 2$ wt.% ($\phi_B \sim 0.017$), which agrees well with the value calculated with Eq. (6).

In Fig. 2 diffusion coefficients (D) of SMA solutions are plotted as a function of polymer volume fraction. D were obtained by cumulant analysis of $g_T^{(1)}(t)$ [45]. Below c^* D slightly increases with increasing concentration, which is typical for the dilute regime. Since the crossover between dilute and semi-dilute state is rather broad due to the polydispersity of the SMA copolymer, a power law was estimated for $\phi_B > 0.017$.

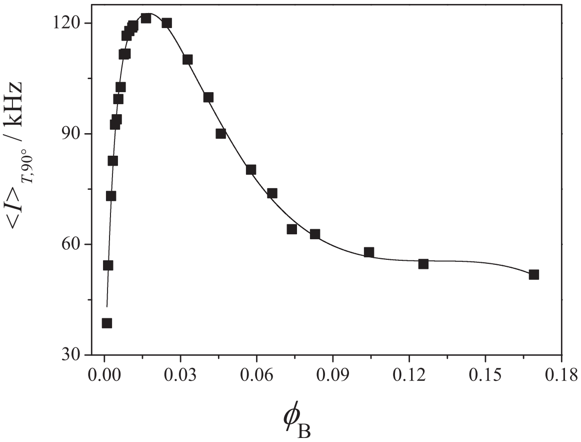

Fig. 1. Scattering intensities of poly(styrene-*co*-maleic anhydride) solutions measured at scattering angle of 90° in dependence of the polymer volume fraction.

The increase of D above c^* can be fitted by: $D \sim \phi_B{}^a$ with $a = 0.6$. For polystyrene in toluene an exponent of 0.65 was found by several authors [46–49]. Moreover, it was shown that even for narrowly distributed polystyrenes a is dependent on the chosen concentration range [47]. The deviation from the theoretical predicted value ($a = 0.75$ [50]) is explained by an increase of the effective solvent viscosity caused by a counter motion of the solvent induced by the motion of the polymers [46,51]. For the present system also the solvent quality has to be taken into account. Dioxane is not a good solvent either for pure PS or maleic anhydride but it acts as suitable solvent for the SMA copolymer exhibiting a medium polarity. The non-attractive interactions with both components may reduce the solvent quality which causes a lower exponent of the power law.

4.2. Synthesis of PS-co-MA networks

A generalized reaction scheme of the cross-linking reaction is given in Fig. 3. EG molecules react with MA groups of individual polymer chains. Due to the bi-functionality of EG, each EG molecule

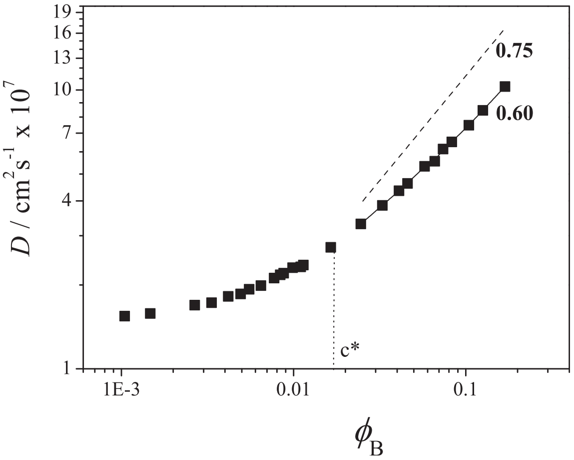

Fig. 2. Diffusion coefficients of poly(styrene-*co*-maleic anhydride) solutions measured at scattering angle of 90° in dependence of the polymer volume fraction. The solid line corresponds to a linear fit of the data in the semi-dilute regime. The theoretical curve as predicted by scaling theory is presented as dashed line. The dotted line indicates c^* as calculated from the scattering intensity (see Fig. 1).

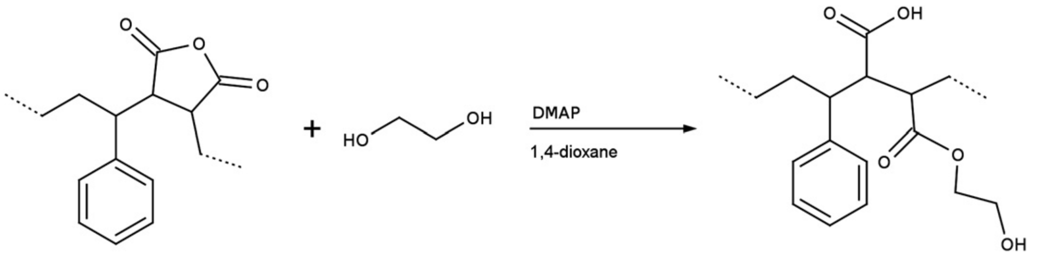

Fig. 3. Generalized scheme of the cross-linking reaction of poly(styrene-*co*-maleic anhydride) with ethylene glycol.

can react with a second MA group. If the second MA group belongs to another polymer chain, two chains are connected and a cross-link point is formed. During the reaction branched molecules of increasing molecular weight and size are formed, which are interconnected to a continuous network at the gel point. A detailed characterization of the cross-linking intermediates in dependence of the polymer and cross-linker concentration can be found in a separate publication [52].

Samples that did not show macroscopic gelation after 2 weeks were not analyzed. The lowest SMA concentration at which networks were obtained was 7.5 wt.%, which is far above c^* of 2 wt. %. Since the cross-linking reaction proceeds very slowly, solutions with lower SMA concentrations may have turned into networks after longer reaction times. Furthermore, the samples 7.5_0.1, 7.5_0.25, and 10_0.1 did not cross-link after 2 weeks due to the low cross-linker concentration. All other samples turned into transparent networks with gel contents in the range of 80–95%.

The volume swelling ratios Q_V of the networks were calculated according to Eq. (7), where ρ_A and ρ_B are the densities of the swelling agent and the network, respectively. For ρ_B the density of SMA was used ($\rho_B = 1.27$ g/cm^3).

$$Q_V = 1 + (Q_m - 1)\frac{\rho_B}{\rho_A} \tag{7}$$

Q_m is the mass related swelling ratio which was determined by weighting disk-shaped gel samples in the swollen state (m_{sw}) and after drying (m_{dry}).

$$Q_m = \frac{m_{sw}}{m_{dry}} \tag{8}$$

In Fig. 4 Q_V is plotted as a function of polymer volume fraction after synthesis ($\phi_{B,\ 0}$) and cross-linker ratio. With increasing polymer concentration Q_V decreases, indicating an increase of cross-linking density. This behavior is also observed in monomer-cross-linked systems [9]. The ratio of MA to EG has no significant influence on Q_V. Only very low EG concentrations lead to an increase of Q_V because less cross-links are formed, resulting in low cross-linking densities. If an excess of EG is used a slight increase of Q_V could be expected. At high EG concentrations less EG molecules are able to form effective cross-links. More likely, after addition to one MA group, the second OH functionality remains unreacted on the polymer chain. Therefore, the cross-linking density decreases. To verify this assumption uniaxial compression measurements were performed on exemplary gels (not shown). They confirmed decreasing cross-linking densities for gels made with EG excess.

A comparison of the polymer volume fraction in the swelling equilibrium ($\phi_B = 1/Q_V$) with $\phi_{B,\ 0}$ revealed that the gels do not swell much after synthesis. Calculated ratios of $\phi_B/\phi_{B,\ 0}$ indicates that the polymer concentration at preparation determines the degree of swelling. $\phi_B/\phi_{B,\ 0}$ is in the range of 1.2–2 for most gels (see Table 1).

4.3. Cooperative diffusion coefficients

Fig. 5 shows D_{coop} as a function of polymer volume fraction (A) and cross-linker ratio (B) of the PS-*co*-MA networks in the preparation state. The concentration dependence of D_{coop} in the studied range can be described by a scaling law: $D_{coop} \sim \phi_B^{0.72}$. Even though a discussion on power law behavior in the narrow concentration range is not meaningful, the differences between solutions and gels can be qualitatively discussed. For the uncross-linked SMA solutions an exponent of 0.60 is observed. Since the exponent represents the solvent quality one may speculate, that the cross-linking of SMA with EG leads to an increase of the solvent-polymer interactions. A reason for this can be found in the chemical nature before and after cross-linking. Polar groups are introduced during the reaction, leading to an enhanced polarity of the network. The interactions with the solvent are therefore enhanced as well. This assumption could be confirmed by an estimation of the solubility parameters [53–55].

However, D_{coop} is reduced during cross-linking. In comparison to the SMA solutions an average decrease of D_{coop} of about 58%

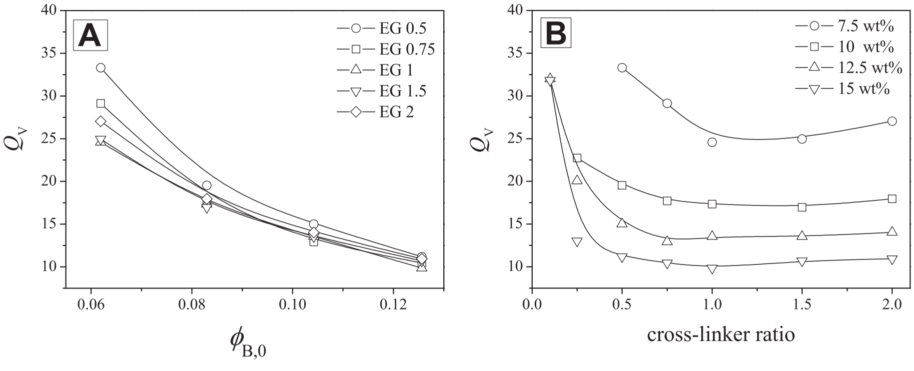

Fig. 4. Volume swelling ratio as function of the polymer volume fraction after synthesis (A) and the cross-linker ratio (B).

Table 1
Ratio of the polymer volume fraction of the swelling equilibrium ϕ_B to that of the preparation state $\phi_{B,\,0}$.

sample	$\frac{\phi_B}{\phi_{B,0}}$	sample	$\frac{\phi_B}{\phi_{B,0}}$
7.5_0.1	[a]	12.5_0.1	3.3
7.5_0.25	[a]	12.5_0.25	2.1
7.5_0.5	2.1	12.5_0.5	1.6
7.5_0.75	1.8	12.5_0.75	1.4
7.5_1	1.5	12.5_1	1.4
7.5_1.5	1.6	12.5_1.5	1.4
7.5_2	1.7	12.5_2	1.5
10_0.1	[a]	15_0.1	4.0
10_0.25	1.9	15_0.25	1.6
10_0.5	1.6	15_0.5	1.4
10_0.75	1.5	15_0.75	1.3
10_1	1.4	15_1	1.2
10_1.5	1.4	15_1.5	1.3
10_2	1.5	15_2	1.4

[a] no gels were obtained.

takes place. This corresponds to an increase of the correlation length ξ ($D_{\text{coop}} \sim \xi^{-1}$). It was expected that ξ will not change significantly during the cross-linking since the correlation length of the semi-dilute SMA solutions will correspond to the mesh size of the networks. But, as already discussed, the reaction of SMA with EG molecules leads to an increase of the solvent–polymer interaction resulting in an expansion of the SMA chains. Furthermore, the introduction of permanent cross-links decreases the osmotic pressure Π [32]. The scaling relationship between Π and ξ ($\Pi \sim \xi^{-3}$) [50] results in an increase of ξ. The reduction of D_{coop} therefore origins from the increased polymer-solvent interactions and the osmotic pressure changes during cross-linking. Similar results were obtained for cross-linked PS chains [32].

The cross-linker concentration has no influence on D_{coop} as can be seen in Fig. 5, B. The cooperative motion therefore is mainly defined by the dynamics of the corresponding polymer solutions. In contrast, Liu and Oppermann reported on increasing D_{coop} with increasing cross-linker concentration. Their networks consisted of modified PS chains cross-linked by therephtaldialdehyde [14]. The cross-linking could be achieved with lower polymer and cross-linker concentrations compared to the PS-*co*-MA system (approx. 1–5 wt.% polymer concentration and a cross-linker ratio of 1:1–1:7). The cross-linking reaction was carried out for several days but no specific reaction time was given. Most likely, due to different reaction kinetics, a cross-linking could be achieved at significant lower polymer concentrations. Contrary to the present system, an increase of the cross-linker concentration resulted in an increase of the cross-linking density. The additional cross-links may result in higher restoring forces and thus higher diffusion coefficients. However, in monomer cross-linked systems, D_{coop} also only show a week dependence on the cross-linker concentration [6,8].

After investigations of the preparation state the gels were swollen to equilibrium and measured again by DLS (Fig. 6). During swelling, the D_{coop} are reduced which can be attributed to an increase of the mesh size. The decrease of D_{coop} is more pronounced for gels with a higher ratio of $\phi_B/\phi_{B,\,0}$ (see Table 1). If $\phi_B/\phi_{B,\,0}$ is smaller, D_{coop} is only slightly reduced because the mesh size does not change much upon swelling.

The scaling of D_{coop} with the polymer concentration in the swollen state is similar to that of the preparation state. However, a power law of $D_{\text{coop}} \sim \phi_B^{0.96}$ can be fitted for the whole concentration range. Neglecting the values at high concentrations an exponent of 0.77 is obtained. Since the differences of ϕ_B and $\phi_{B,\,0}$ for this samples are very small, some inaccuracy has to be taken into account. Furthermore, because of the narrow concentration range, a quantitative discussion of power law changes is not meaningful. A linear increase of D_{coop} with increasing polymer concentration is observed as typical for semi-dilute polymer solutions. The scaling can be roughly considered as the same as in the preparation state.

Similar to the preparation state the cross-linker concentration has no significant influence on D_{coop} in the swollen state. A maximum can be observed for all networks made with a cross-linker ratio of MA to EG of 1:1. For increasing polymer concentrations this maximum becomes more pronounced. Gels made with a cross-linker ratio of 1:1 exhibit the lowest volume changes by going from preparation state to swelling equilibrium. The low expansion causes only a slight increase of the mesh size. Networks made with higher or lower cross-linker concentration show higher volume changes and therefore a more distinct increase of the mesh size. The maximum in the curves represents the differences of the relative changes of the mesh sizes.

4.4. *Network inhomogeneities*

DLS experiments were performed at different sample positions to evaluate D_{coop} and $\langle I_F \rangle_T$. On each sample position $\langle I \rangle_T$ was measured. An averaging over all sample position gives the ensemble-average scattering intensity $\langle I \rangle_E$ which is often referred as quantity for inhomogeneities [2]. However, homogeneous ergodic microgel dispersions showed even higher $\langle I \rangle_E$ values as their corresponding hybrid gels [40]. Therefore, the ratio of $\langle I_F \rangle_T$ to $\langle I \rangle_E$ is more likely to reflect the extent of inhomogeneity of a given system, not the value of $\langle I \rangle_E$ alone.

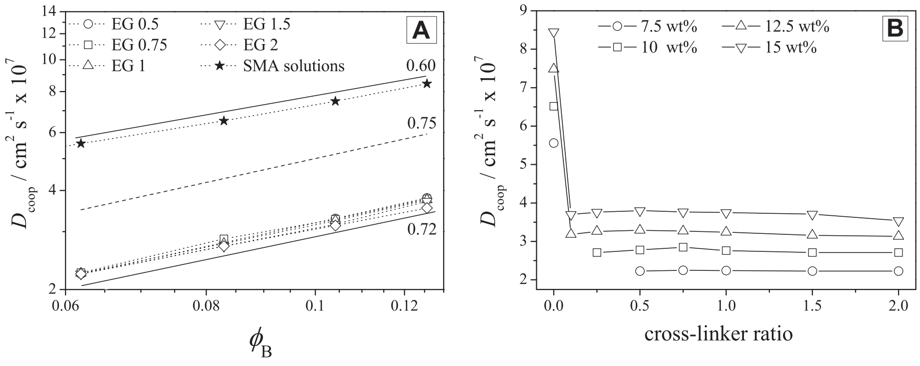

Fig. 5. Cooperative diffusion coefficients D_{coop} measured in the preparation state as a function of the polymer volume fraction (A) and the cross-linker ratio (B). In (A): Data for SMA solutions were taken from Fig. 2. Dotted lines are drawn as guide to the eye. Dashed line was plotted according to $D_{\text{coop}} \sim \phi_B^{0.75}$. Solid lines are plottet according to $D_{\text{coop}} \sim \phi_B^{0.72}$ and $D_{\text{coop}} \sim \phi_B^{0.60}$.

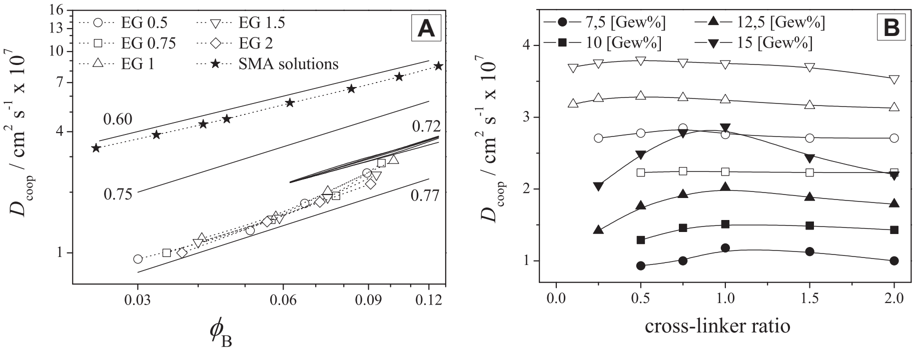

Fig. 6. Cooperative diffusion coefficients D_{coop} measured in the fully swollen state as a function of the polymer volume fraction (A) and the cross-linker ratio (B). In (A): Data for SMA solutions were taken from Fig. 2. Solid lines were plottet according to $D_{coop} \sim \phi_B{}^a$, $a = 0.60, 0.75, 0.77$. Data obtained for the preparation state are added as line graph ($D_{coop} \sim \phi_B^{0.72}$). In (B): filled and open symbols correspond to swollen and preparation state, respectively.

4.4.1. Preparation state

Fig. 7 shows $\langle I\rangle_E$ and $\langle I_F\rangle_T$ as a function of polymer concentration for gels in the preparation state. Also included are the intensity data for the corresponding polymer solutions $\langle I\rangle_{sol}$.

$\langle I_F\rangle_T$ decreases with increasing polymer concentration over the entire range. The concentration dependence of $\langle I_F\rangle_T$ can be roughly regarded as independent on the cross-linker ratio, since it can be described by one function. Both cross-linker and polymer concentration dependence of $\langle I_F\rangle_T$ are in agreement with the results obtained by Liu and Oppermann [14]. The dynamic fluctuations are only influenced by the polymer concentration representing the dynamics of the corresponding SMA solutions.

With increasing polymer concentration the difference between $\langle I_F\rangle_T$ and $\langle I\rangle_{sol}$ becomes more pronounced. Since the solvent quality is changed during the cross-linking reaction as discussed in Sec. 4.3, $\langle I_F\rangle_T$ can not be expected to exhibit the same values as $\langle I\rangle_{sol}$, but the stronger decrease of $\langle I_F\rangle_T$ may indicate that concentration fluctuations are suppressed at high ϕ_B.

With increasing polymer volume fraction up to 0.105 (12.5 wt.%) $\langle I\rangle_E$ decrease. In comparison to $\langle I\rangle_{sol}$, $\langle I\rangle_E$ is only slightly increased. For the highest cross-linker concentration (EG 2) $\langle I\rangle_E$ even equals $\langle I\rangle_{sol}$, indicating that for polymer concentrations $\leq$ 12 wt.% no distinct static component is present in the networks. However, as mentioned above, due to changes of the solvent quality this conclusion can not be drawn out of a comparison of $\langle I\rangle_E$ to $\langle I\rangle_{sol}$. In fact, only the relation of $\langle I_F\rangle_T$ to $\langle I\rangle_E$ contains information about the extent of the static structure. Going to higher concentrations $\langle I\rangle_E$ rises while $\langle I_F\rangle_T$ decreases indicating that additional scattering contributes to $\langle I\rangle_E$.

This effect can be discussed in more detail by plotting the contribution of the dynamic fluctuations to the ensemble scattering intensity ($\langle I_F\rangle_T/\langle I\rangle_E$) as a function of the polymer concentration as shown in Fig. 8. At the highest polymer concentration dynamic fluctuations contribute less than 50% to the scattering intensity, indicating that more than 50% origin from static contributions. Gels made with lower polymer concentrations exhibit ratios of $\langle I_F\rangle_T$ to $\langle I\rangle_E$ in the range of 50–90%, which decrease with increasing polymer concentration. It can be concluded that the cross-linking causes a slight increase of $\langle I\rangle_E$ due to the introduction of cross-links and that $\langle I_F\rangle_T$ decreases because of some restrictions of the dynamic fluctuation due to that cross-links.

Theoretically, homogeneous networks will always exhibit $\langle I_F\rangle_T/\langle I\rangle_E$ values smaller than unity because cross-links are present in the structure even if they are homogeneously distributed. A higher cross-linking density should therefore result in smaller ratios because the static component is increased. For the present system the cross-linking density increases with increasing polymer concentration, as could be concluded out of the swelling ratios and uniaxial compression tests. By increasing the polymer concentration from 7.5 wt.% to 10 wt.% Q_V decreases significantly (see Fig. 4) while $\langle I_F\rangle_T/\langle I\rangle_E$ decreases only slightly. Even when more cross-links are present, the dynamic contribution did not change significantly. This means, that the cross-links are distributed homogeneously in

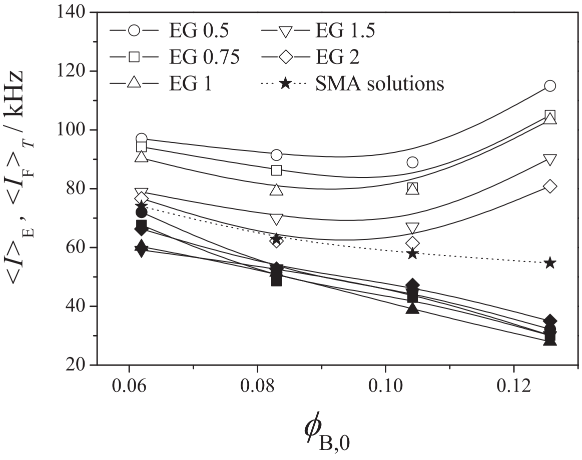

Fig. 7. Ensemble-average scattering intensity $\langle I\rangle_E$ and fluctuating component of the scattering intensity $\langle I_F\rangle_T$ of PS-*co*-MA networks in the preparation state as functions of the polymer volume fraction. Filled symbols: $\langle I_F\rangle_T$, open symbols: $\langle I\rangle_E$.

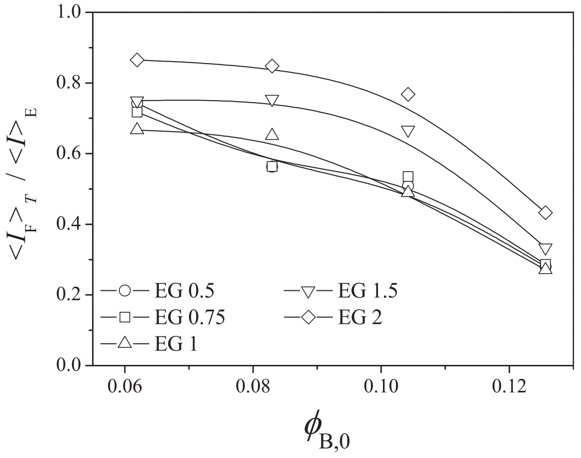

Fig. 8. Ratio of $\langle I_F\rangle_T$ to $\langle I\rangle_E$ of PS-*co*-MA networks in the preparation state as function of the polymer volume fraction.

the network and the concentration fluctuation is not restricted due to local areas of high cross-linking density. Therefore, PS-*co*-MA networks made with low SMA concentrations can be considered as fairly homogeneous. The strong reduction of $\langle I_F\rangle_T/\langle I\rangle_E$ at high SMA concentrations indicates that frozen inhomogeneities are introduced into the network because more than 50% of static contribution can not be attributed to the increased cross-linking density alone. The reason can be found in the limited diffusion of EG molecules at high polymer concentrations which led to the incorporation of highly cross-linked clusters into the network structure.

Liu and Oppermann observed increasing $\langle I\rangle_E$ values with increasing polymer concentration [14]. In their study, the highest polymer concentration was still below the lowest one in the present study. Therefore, a direct comparison is not possible. However, $\langle I\rangle_E$ of their gels reached a plateau value at the highest polymer concentration. One may speculate, that a further increase of the polymer concentration would result in a decrease of $\langle I\rangle_E$, as observed for the PS-*co*-MA networks. $\langle I_F\rangle_T/\langle I\rangle_E$ decreased with increasing polymer concentration, which must be attributed to the significant lower concentration range.

The influence of the cross-linker concentration on $\langle I_F\rangle_T$, $\langle I\rangle_E$ and the ratio of $\langle I_F\rangle_T$ to $\langle I\rangle_E$ will not be shown graphically because most information can be derived from Figs. 7 and 8. Increasing the cross-linker concentration usually leads to an increase of the cross-linking density. For the PS-*co*-MA gels this can be observed up to a ratio of MA to EG of 1:0.5. A further increase of EG concentrations results in less dense networks as discussed in Sec. 4.2. $\langle I\rangle_E$ is affected by the cross-linking density and increases up to MA:EG of 1:0:5. At higher cross-linker concentrations $\langle I\rangle_E$ decreases. $\langle I\rangle_E$ can therefore be related to the amount of cross-links.

$\langle I_F\rangle_T$ is not affected by the cross-linker concentration. The dynamic fluctuations are solely determined by the polymer concentration. $\langle I_F\rangle_T/\langle I\rangle_E$ is mainly characterized by the maximum of $\langle I\rangle_E$ for gels with the highest cross-linking density but the influence is not significant.

Out of the results of the preparation state one can conclude that random cross-linking of SMA solutions can lead to homogeneous networks as long as the polymer concentration is below 12 wt.% and an excess of EG is used. At higher SMA concentrations heterogeneities are introduced during cross-linking. The concentration fluctuations are predominantly determined by the dynamics of the network chains, which are similar to those in the corresponding polymer solution.

4.4.2. *Swollen state*

During the swelling process one would expect a decrease of the scattering intensity due to the dilution of the network and the reduction of the scattering elements. Experimental results did not support this assumption. The scattering intensity in general increases by going to swelling equilibrium [9,56]. An explanation of this phenomenon was given by the model of frozen blobs [57]. A frozen blob is formed by introducing chemical neighbor junctions (domains of high cross-linking density). In the preparation state one can not distinguish between domains of high and low cross-linking density since the gel is characterized by the concentration of the corresponding polymer solution. Therefore, in the preparation state the network inhomogeneities are hidden by the neighboring networks chains and the gels appear homogeneous. When swelling, it will be difficult to move the cross-links of a frozen blob apart from each other. In contrast, domains of low cross-linking density swell much more and the inhomogeneity becomes pronounced. Therefore, the PS-*co*-MA networks were swollen to equilibrium and analyzed again by dynamic light scattering.

As can be seen in Fig. 9 $\langle I_F\rangle_T$ increased upon swelling following the trend of the SMA solutions. The concentration dependence can be described by one function independent on the cross-linker concentration. This proves that $\langle I_F\rangle_T$ indeed represents the dynamic fluctuations of the networks chains which corresponds to the behavior of semi-dilute solutions. For some samples $\langle I_F\rangle_T$ values that are higher than $\langle I\rangle_{sol}$ are obtained. This will not be discussed physically, since it may be attributed to an overestimation of $\langle I_F\rangle_T$ in the extrapolation (Eq. (5)) due to some limited accuracy of the evaluation.

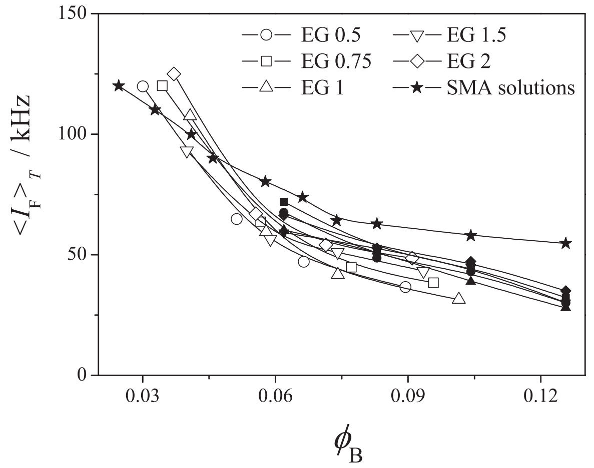

Fig. 9. Fluctuating component of the scattering intensity $\langle I_F\rangle_T$ of PS-*co*-MA networks in the preparation state (filled symbols) and the swelling equilibrium (open symbols) as function of the polymer volume fraction. Data for SMA solutions were taken from Fig. 1.

$\langle I\rangle_E$ markedly increased upon swelling (Fig. 10). Remembering that the volume change of the PS-*co*-MA is not very pronounced (see Table 1), it is astonishing that $\langle I\rangle_E$ at least doubled for all networks. $\langle I\rangle_E$ decreases with increasing polymer concentration showing semi-dilute behavior. In comparison to $\langle I\rangle_{sol}$ of the corresponding SMA solution, $\langle I\rangle_E$ is much higher. Since $\langle I_F\rangle_T$ only slightly increased upon swelling, representing very well $\langle I\rangle_{sol}$ (Fig. 9), the increase of $\langle I\rangle_E$ has to be attributed to an increase of the static component and therefore to an increase of the inhomogeneity.

Fig. 11 clearly supports this assumption. The dynamic contribution to the ensemble scattering intensity is drastically reduced upon swelling, to only 10–20%. $\langle I\rangle_E$ is mainly affected by a strong static component arising from the network heterogeneity. It can be concluded that a gel prepared by random-cross-linking of long

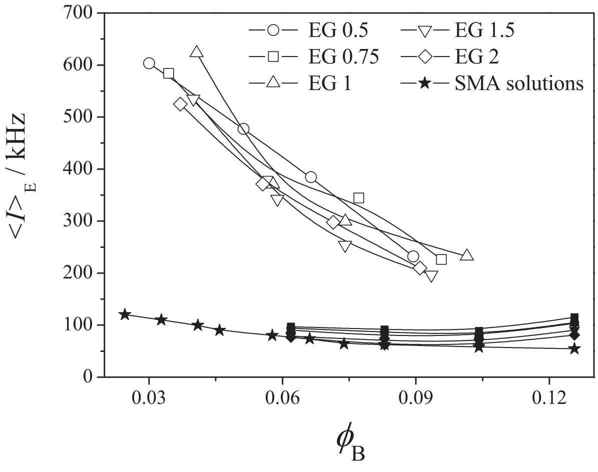

Fig. 10. Ensemble-average scattering intensity $\langle I\rangle_E$ of PS-*co*-MA networks in the preparation state (filled symbols) and the swelling equilibrium (open symbols) as function of the polymer volume fraction. Data for SMA solutions were taken from Fig. 1.

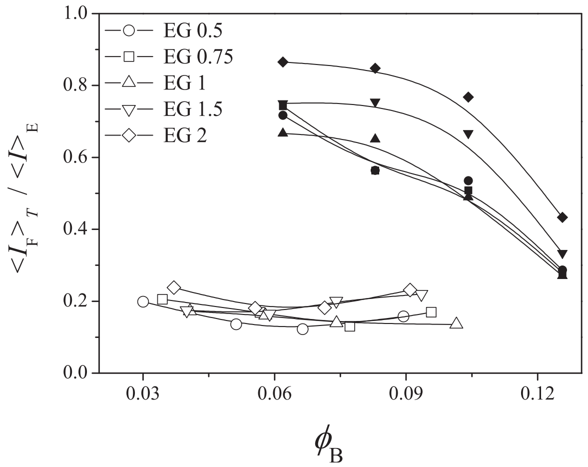

Fig. 11. Ratio of $\langle I_F \rangle_T$ to $\langle I \rangle_E$ of PS-*co*-MA networks in the preparation state (filled symbols) and the swelling equilibrium (open symbols) as function of the polymer volume fraction.

chains exhibit large scale fractal heterogeneities when swollen to equilibrium, even when the reaction has been stopped far beyond the gel point. This results from a natural fluctuation of the cross-linking density always occurring in the reaction bath.

Out of Figs. 9–11 one can see that the cross-linker concentration has no influence on the heterogeneity. In general, for monomer cross-linked systems, an increase of the heterogeneity is observed with increasing cross-linker concentration due to an increase of the cross-linking density [8,26]. For the PS-*co*-MA networks the cross-linking density only slightly varies with the cross-linker concentration resulting in a weak influence on the heterogeneity.

The results of the swelling equilibrium show that the concentrations dependence of $\langle I \rangle_E$, $\langle I_F \rangle_T$ and $\langle I_F \rangle_T / \langle I \rangle_E$ can be described by master curves. This strongly indicates that random cross-linked networks exhibit self-similar structures with respect to the polymer concentration [36]. The analysis of structural formations during the cross-linking reaction was published elsewhere [52].

5. Conclusions

Networks based on poly(styrene-*co*-maleic anhydride) and ethylene glycol were synthesized by random cross-linking of semi-dilute solutions. The cooperative diffusion and the network inhomogeneities were investigated by dynamic light scattering of the gels in the preparation state as well as in the swelling equilibrium. Influences of the cross-linker concentration and the polymer volume fraction on the gel characteristics were analyzed.

The polymer concentration dependence of the cooperative diffusion coefficients D_{coop} can be described by a power law as typical for semi-dilute polymer solutions: $D_{\text{coop}} \sim \varphi_B{}^a$ with a being 0.72 and 0.77 for the preparation state and the swelling equilibrium, respectively. In comparison to the uncross-linked poly (styrene-*co*-maleic anhydride) solutions ($a = 0.60$) a was increased due to increased solvent-polymer interactions in the networks. The cross-linker concentration has no influence on the cooperative motion.

The heterogeneity of the networks could be characterized in terms of the ensemble-averaged scattering intensity $\langle I \rangle_E$, the fluctuating component of the scattering intensity $\langle I_F \rangle_T$ and the ratio of $\langle I_F \rangle_T$ to $\langle I \rangle_E$. In the preparation state as well as in the swelling equilibrium $\langle I_F \rangle_T$ resembles very much the scattering intensity of the corresponding polymer solutions. The thermal concentration fluctuations remain in the system after cross-linking and are solely determined by the polymer volume fraction.

Additional to the dynamic component, $\langle I \rangle_E$ also includes static contributions. In the preparation state the static component of $\langle I \rangle_E$ is not very pronounced and particularly, networks made with low polymer concentration, appear homogeneous. The situation changed after swelling the gels to equilibrium. $\langle I \rangle_E$ drastically increased while decreasing the dynamic contributions to 10–20%. This can be directly attributed to large inhomogeneities present in the gel structure. Therefore, the strategy of synthesizing homogeneous gels by applying random cross-linking is not applicable.

The cross-linker concentration has only minor influence on the inhomogeneity. Moreover, in the swollen state $\langle I \rangle_E$, $\langle I_F \rangle_T$ and $\langle I_F \rangle_T / \langle I \rangle_E$ are functions of the polymer concentration, independent of the cross-linker amount, showing that scaling laws may be transferred onto networks.

References

[1] Ikkai F, Shibayama M. Inhomogeneity control in polymer gels. J Polym Sci Pol Phys 2005;43:617–28.
[2] Shibayama M. Spatial inhomogeneity and dynamic fluctuations of polymer gels. Macromol Chem Phys 1998;199:1–30.
[3] Joosten JGH, McCarthy JL, Pusey PN. Dynamic and static light scattering by aqueous polyacrylamide gels. Macromolecules 1991;24:6690–9.
[4] Fang L, Brown W. Dynamic light scattering by permanent gels: heterodyne and nonergodic medium methods of data evaluation. Macromolecules 1992;25:6897–903.
[5] Shibayama M, Taekeuchi T, Nomura S. Swelling shrinking and dynamic light-scattering-studies on chemically cross-linked poly(vinyl alcohol) gels in the presence of borate ions. Macromolecules 1994;27:5350–8.
[6] Moussaid A, Candau SJ, Joosten JGH. Structural and dynamic properties of partially charged poly(acrylic acid) gels: nonergodicity and inhomogeneities. Macromolecules 1994;27:2102–10.
[7] Skouri R, Schosseler F, Munch JP, Candau SJ. Swelling and elastic properties of polyelectrolyte gels. Macromolecules 1995;28:197–210.
[8] Shibayama M, Norisuye T, Nomura S. Cross-link density dependence of spatial inhomogeneities and dynamic fluctuations of poly(N-isopropylacrylamide) gels. Macromolecules 1996;29:8746–50.
[9] Shibayama M, Shirotani Y, Shiwa Y. Static inhomogeneities and dynamics of swollen and reactor-batch polymer gels. J Chem Phys 2000;112:442–9.
[10] Rodd AB, Dunstan DE, Boger DV, Schmidt J, Burchard W. Heterodyne and nonergodic approach to dynamic light scattering of polymer gels: aqueous xanthan in the presence of metal ions (aluminum(III)). Macromolecules 2001;34:3339–52.
[11] Norisuye T, Kida Y, Masui N, Tran-Cong-Miyata Q, Maekawa Y, Yoshida M, et al. Studies on two types of built-in inhomogeneities for polymer gels: frozen segmental concentration fluctuations and spatial distribution of cross-links. Macromolecules 2003;36:6202–12.
[12] Ngai T, Wu C, Chen Y. Origins of the speckles and slow dynamics of polymer gels. J Chem Phys 2004;108:5532–40.
[13] Norisuye T, Tran-Cong-Miyata Q, Shibayama M. Dynamic inhomogeneities in polymer gels investigated by dynamic light scattering. Macromolecules 2004;37:2944–53.
[14] Liu R, Oppermann W. Spatial inhomogeneities of polystrene gels prepared from semi-dilute solutions. Macromolecules 2006;39:4159–67.
[15] Matsunaga T, Sakai T, Akagi Y, Chung U, Shibayama M. Structure characterization of tetra-PEG gel by small-angle neutron scattering. Macromolecules 2009;42(4):1344–51.
[16] Naghash HJ, Okay O. Formation and structure of polyacrylamide gels. J Appl Polym Sci 1996;60:971–9.
[17] Patras G, Qiao GG, Solomon DH. Controlled formation of microheterogeneous polymer networks: influence of monomer reactivity on gel structure. Macromolecules 2001;34:6396–401.
[18] Mallam S, Horkay F, Hecht AM, Geissler E. Scattering and swelling properties of inhomogeneous polyacrylamide gels. Macromolecules 1989;22:3356–61.
[19] Fang L, Brown W. Decay time distributions from dynamic light scattering for aqueous poly(vinyl alcohol) gels and semi-dilute solutions. Macromolecules 1990;23:3284–90.
[20] Konak C, Jakes J, Brown W, Fang L. Dynamic light scattering from polymer solutions and gels at the gelation threshold. Polymer 1991;32:1077–9.
[21] Horkay F, Burchard W, Hecht AM, Geissler E. Scattering properties of poly (vinyl acetate) gels in different solvents. Macromolecules 1993;26:4203–7.
[22] Geissler E. Dynamic light scattering. Oxford: Clarendon Press; 1993. Ch. Dynamic light scattering from polymer gels., pp. 471–511.
[23] Hecht A-M, Horkay F, Schleger P, Geissler E. Thermal fluctuations in polymer gels investigated by neutron spin echo and dynamic light scattering. Macromolecules 2002;35:8552–5.
[24] Furukawa H, Horie K, Nozaki R, Okada M. Swelling-induced modulation of static and dynamic fluctuations in polyacrylamide gels observed by scanning microscopic light scattering. Phys Rev E Stat 2003;68. 031406/1–031406/14.

[25] Richter S, Boyko V, Schroeter K. Gelation studies on a radical chain cross-linking copolymerization process: comparison of the critical exponents obtained by dynamic light scattering and rheology. Macromol Rapid Commun 2004;25:542–6.

[26] Shibayama M. Universality and specificity of polymer gels viewed by scattering methods. Bull Chem Soc Jpn 2006;79:1799–819.

[27] Miyazaki S, Endo H, Karino T, Haraguchi K, Shibayama M. Gelation mechanism of poly(N-isopropylacrylamide)-clay nanocomposite gels. Macromolecules 2007;40:4287–95.

[28] Ferse B, Richter S, Eckert F, Kulkarni A, Papadakis CM, Arndt K-F. Gelation mechanism of poly(N-isopropylacrylamide)-clay nanocomposite hydrogels synthesized by photopolymerization. Langmuir 2008;24:12627–35.

[29] Arndt KF, Schmidt T, Menge H. Poly (vinyl methyl ether) hydrogel formed by high energy irradiation. Macromol Symp 2001;164:313–22.

[30] Ulanski P, Pawlowska W, Kadlubowski S, Henke A, Gottlieb R, Arndt KF, et al. Synthesis of hydrogels by radiation-induced cross-linking of pluronic® F127 in $N_2$0-saturated aqueous solution. Polym Adv Technol 2006;17:804–13.

[31] Gottlieb R, Kaiser C, Gohs U, Arndt KF. Temperature sensitive hydrogels based on hydroxypropylcellulose by high energy irradiation. Macromol Symp 2007;254:361–9.

[32] Mendes E, Linder P, Buzier M, Boué F, Bastide J. Experimental-evidence for inhomogeneous swelling and deformation in statistical gels. Phys Rev Lett 1991;66:1595–8.

[33] Ramzi A, Zielinski F, Bastide J, Boué F. Butterfly patterns - small-angle neutron-scattering from deuterated mobile chains in a randomly cross-linked polystyrene network. Macromolecules 1995;28:3570–87.

[34] Geoghegan M, Boue F, Bacri G, Menelle A, Bucknall DG. A neutron reflectometry study of polystyrene network interfaces. Eur Phys J B 1998;3:83–96.

[35] Norisuye T, Masui N, Kida Y, Ikuta D, Kokufuta E, Ito S, et al. Small angle neutron scattering studies on structural inhomogeneities in polymer gels: irradiation cross-linked gels vs chemically cross-linked gels. Polymer 2002;43:5289–97.

[36] Matsunaga T, Sakai T, Akagi Y, Chung UI, Shibayama M. SANS and SLS studies on tetra-arm PEG gels in as-prepared and swollen states. Macromolecules 2009;42(16):6245–52.

[37] Sakai T, Matsunaga T, Yamamoto Y, Ito C, Yoshida R, Suzuki S, et al. Design and fabrication of a high-strength hydrogel with ideally homogeneous network structure from tetrahedron-like macromonomers. Macromolecules 2008;41(14):5379–84.

[38] Ngai T, Wu C, Chen Y. Effects of temperature and swelling on chain dynamics during the solgel transition. Macromolecules 2004;37:987–93.

[39] Kuru EA, Orakdogen N, Okay O. Preparation of homogeneous polyacrylamide hydrogels by free-radical crosslinking copolymerization. Eur Polym J 2007;43(7):2913–21.

[40] Zhao Y, Zhang GZ, Wu C. Nonergodic dynamics of a novel thermally sensitive hybrid gel. Macromolecules 2001;34(22):7804–8.

[41] Wu C. Laser light scattering characterization of special intractable macromolecules in solution. Adv Polym Sci 1998;137:103–34.

[42] Pusey P, Van Megen W. Dynamic light scattering by non-ergodic media. Physica A 1989;157:705–41.

[43] des Cloizeaux J, Jannink G. Polymers in solution: their modelling and structure. Oxford: Clarendon Press; 1990.

[44] Nose T, Chu B. Static and dynamical properties of polystyrene in trans-decalin. 1. NBS 705 standard near θ-conditions. Macromolecules 1979;12:590–9.

[45] Koppel DE. Analysis of macromolecular polydispersity in intensity correlation spectroscopy – method of cumulants. J Chem Phys 1972;57(11):4814–20.

[46] Nemoto N, Makita Y, Tsunashima Y, Kurata M. Dynamic light-scattering of polymer-solutions .4. semidilute solutions of polystyrenes and their binary blends in benzene. Macromolecules 1984;17(12):2629–33.

[47] Wiltzius P, Haller HR, Cannell DS, Schaefer DW. Dynamics of long-wavelength concentration fluctuations in solutions of linear-polymers. Phys Rev Lett 1984;53(8):834–7.

[48] Zhang KJ, Briggs ME, Gammon RW, Sengers JV, Douglas JF. Thermal and mass diffusion in a semidilute good solvent-polymer solution. J Chem Phys 1999;111(5):2270–82.

[49] Harnau L. Influence of intermolecular interaction on the dynamics of good solvent-polymer solutions. J Chem Phys 2001;115(4):1943–5.

[50] de Gennes P-G. Scaling concepts in polymer physics. Ithaca, NY: Cornell University Press; 1979.

[51] Zettl U, Hoffmann ST, Koberling F, Krausch G, Enderlein J, Harnau L, et al. Self-diffusion and cooperative diffusion in semidilute polymer solutions as measured by fluorescence correlation spectroscopy. Macromolecules 2009;42(24):9537–47.

[52] Krüger S, Krahl F, Arndt K-F. Random cross-linked poly(styrene- *co*-maleic anhydride): characterization of cross-linking intermediates by size exclusion chromatography. Eur Polym J; 2010;. doi:10.1016/j.eurpolymj.2010.01.024.

[53] Ng SC, Chee KK. Solubility parameters of copolymers as determined by turbidimetry. Eur Polym J 1997;33(5):749–52.

[54] Grulke EA. Polymer handbook. 4th ed. Wiley & Sons; 1999. Ch. Solubility Parameter Values, pp. VII/675–VII/714.

[55] The solubility parameters δ of dioxane and SMA are 20.4 and 18.9 (MPa)$^{0.5}$, respectively. δ of the networks can be calculated from the sum of the products of the component solubility parameters with their volume fractions. Therefore, by cross-linking SMA with EG δ increase. For the different ratios of EG to MA following values (in (MPa)$^{0.5}$) were obtained: EG 0.5: 19.6; EG 0.75: 20.0 EG 1: 20.3; EG 1.5; 20.8, EG 2: 21.3. For a good solvent quality, δ of the polymer or network should equal the value of the solvent. Since δ of the networks is similar to dioxane, a better solvent quality can be concluded.

[56] Kizilay MY, Okay O. Effect of swelling on spatial inhomogeneity in poly(acrylamide) gels formed at various monomer concentrations. Polymer 2004;45(8):2567–76.

[57] Bastide J, Leibler L. Large-scale heterogeneities in randomly cross-linked networks. Macromolecules 1988;21:2647–9.